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NMR Spectroscopic Group Analysis, Using Bituminous Coals as Example

H.H. OELERT

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Summary. Problems of high-resolution NMR spectroscopy in the field of multicomponent analysis are discussed. A table of signal positions for protons in hydrocarbons is given. The possibility of quantitative work is pointed out. Combining measurements of ultimate analysis, IR and NMR spectroscopy a method for the estimation of carbon distribution in various structural groups is worked out. The results of some extracts of bituminous coals are presented.

Introduction

NMR spectroscopy can be used as broad-line or high-resolution technique for multicomponent analysis. Broad-line NMR has hitherto found limited application. High-resolution NMR has the advantage that the various proton bonds produce characteristic signal positions, but the disadvantage that only substances soluble in suitable solvents can be analyzed. Possible applications in the field of mineral oil analysis have been demonstrated by WILLIAMS (17) and by LUTHER & OELERT (12,13). They showed (12,13) that the method, especially when combined with other measuring techniques, allows detailed group analysis.

This report will discuss the possibilities of analyzing multicomponent mixtures among solid fuels.

Qualitative analysis

The "chemical shifts" occurring in the spectra and given in ppm related to tetramethylsilane (TMS) are characteristic of the bonding state of the protons producing the signals and of the interactions with neighbouring protons.

The literature offers several indications for assigning the signals occurring in the spectra of coal-like substances, for instance in TSCHAMLER & OTH (15), LAHIRI et al. (11), BROWN, LADNER & SHEPPARD (5), and BROOKS & STEVEN (4). The paper by BARTLE & SMITH (1) no doubt has given the most detailed data to date on the absorption ranges of coal-like substances. - When assigning signals from various coal-like substances it can be assumed that a hydrocarbon skeleton exists and that heteroatoms like oxygen, nitrogen, or sulphur in substituents or rings have no dominating

effect on the spectra. Keeping this in mind it seems appropriate at first to establish a general assignment table for all imaginable proton situations in hydrocarbons. For this purpose we analyzed a large number of substances from bituminous coal tar and used data from the literature (6-8,14,16). The Table shown in Figure 1 is based on all these data; it requires a few explicatory comments:

1. The assignment ranges are designed to help in determining relative areas under the lines, with the dissolution conditions normally occurring in complex hydrocarbon mixtures having been taken into account.

2. The breakdown by types of substitution on the benzene ring in analogy to IR spectroscopy applies only to methyl or short-chain alkyl substituents, i.e. where noticeable interaction effects may occur that are further intensified by diamagnetic shielding effects of methyl substituents.

3. The negative shift in higher-condensed aromatics applies only where the resonance effect in coplanar aromatic rings is not compensated or exceeded by inductive or diamagnetic shielding effects.

4. The individual groups of thin lines give an approximate representation of all possible structures which may also contain atoms other than C and H. However, the expected ranges in some cases require additional information regarding shifts due to relatively more electropositive neighbouring groups.

The listed values refer to very low concentrations in a proton-free apolar solvent (e.g. carbon tetrachloride). At higher concentrations the actual positions may differ from those listed. Effects of this nature have been referred to by, among others, POPLE, SCHNEIDER & BERNSTEIN (14 b), BOTHNER-BY & GLICK (3), and BARTLE & SMITH (2). In another study BARTLE & SMITH (1) investi-

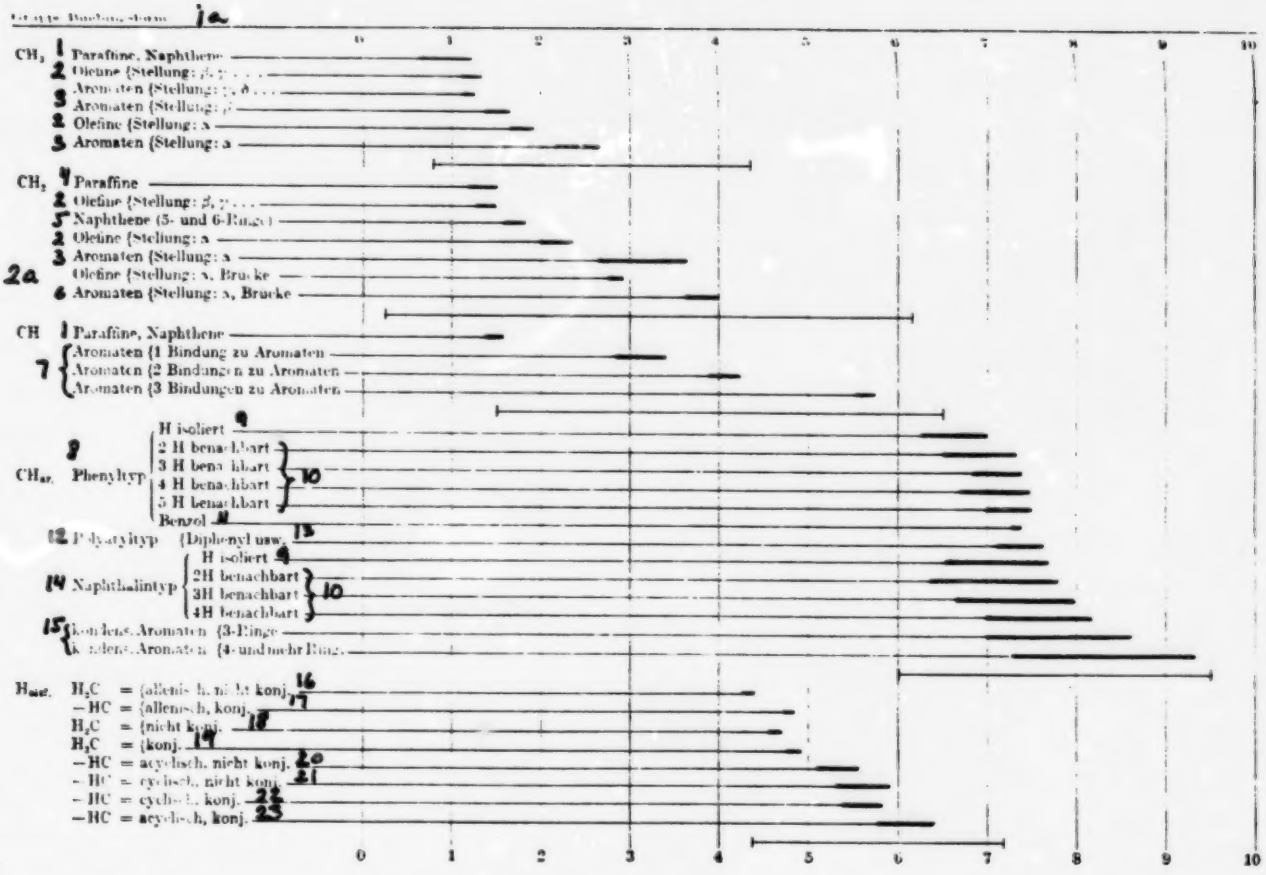
1a
0 1 2 3 4 5 6 7 8 9 10
CH3 1 Paraffine, Naphthene
2 Olefine (Stellung: β, γ . . .
Aromaten (Stellung: γ, δ . . .
3 Aromaten (Stellung: β
2 Olefine (Stellung: α
3 Aromaten (Stellung: α
CH2 4 Paraffine
2 Olefine (Stellung: β, γ . . .
5 Naphthene (5- und 6-Ring-)
2 Olefine (Stellung: α
3 Aromaten (Stellung: α
2a Olefine (Stellung: α, Brücke
6 Aromaten (Stellung: α, Brücke
CH 1 Paraffine, Naphthene
7 Aromaten (1 Bindung zu Aromaten
Aromaten (2 Bindungen zu Aromaten
Aromaten (3 Bindungen zu Aromaten
8 CHar. Phenyltyp H isoliert 9
2 H benachbart
3 H benachbart
4 H benachbart
5 H benachbart 10
Benzol 11
12 Polyaryltyp (Diphenyl usw. 13
14 Naphthalintyp H isoliert 9
2H benachbart
3H benachbart 10
4H benachbart
15 Kondens. Aromaten (3-Ringe
Kondens. Aromaten (4- und mehr Ringe
Holef. H2C = (allenisch, nicht konj. 16
–HC = (allenisch, konj. 17
H2C = (nicht konj. 18
H2C = (konj. 19
–HC = acyclisch, nicht konj. 20
–HC = cyclisch, nicht konj. 21
–HC = cyclisch, konj. 24
–HC = acyclisch, konj. 23
0 1 2 3 4 5 6 7 8 9 10

Figure 1. Assignment of "chemical shifts" in NMR spectra of hydrocarbons

For translation key please see p. 5.

Translation key for Figure 1

1a - group, bond type
1 - paraffins, naphthenes
2a - olefins (position: α, bridge)
2 - olefins (position:...)
3 - aromatics (position:...)
4 - paraffins
5 - naphthenes (5 and 6 rings)
6 - aromatics (position: α, bridge)
7 - aromatics (1/2/3 bonds to aromatics)
8 - phenyl type
9 - H, isolated
10 - 2/3/4/5 H adjacent
11 - benzene
12 - polyaryl type
13 - diphenyl, etc.
14 - naphthalene type
15 - condensed aromatics - 3 rings; 4 and more rings
16 - allenic, not conjugated
17 - allenic, conjugated
18 - not conjugated
19 - conjugated
20 - acyclic, not conjugated
21 - cyclic, not conjugated
22 - cyclic, conjugated
23 - acyclic, conjugated

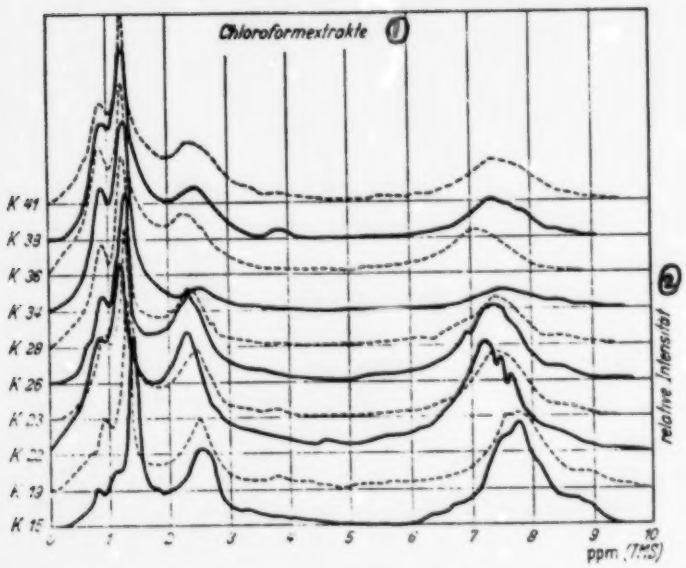

Figure 2. NMR spectra of investigated series of substances

Key: 1 - chloroform extracts
2 - relative intensity

gated in detail the effect of concentration. As an example they used a tar fraction that was measured in carbon disulphide at concentrations of 0 to 20%. They found that for several signals a linear relationship existed between maxima location and concentration, with the chemical shifts decreasing with increasing concentrations. For signals of aromatic protons, deviations of -0.13 to -0.23 ppm were measured, for protons in aromatic alkyl groups, a deviation of -0.1 ppm between infinite dilution and 20% concentration. The signals of non-aromatic alkyl groups remained unaffected. This was confirmed by measurements of our own with lubricating oils (12,13) in which we found that most signal positions remained constant at concentrations between 0 and 30% for carbon tetrachloride and carbon disulphide as solvents. Since, as will be shown below, the assignment ranges for the proton situations of interest here can be delimited against each other with sufficient accuracy, any concentration shifts that may occur can be ignored.

The spectra of the investigated substances (Figure 2) essentially show five signals, in the case of certain substances additional, weaker signals. The maxima of these frequently broad signals lie at 0.8 - 0.9; 1.2 - 1.5; approx. 2.5; 3 - 4.5; and 7 - 8 ppm. According to the assignment table the maxima locations of the signals are assigned as follows:

0.8 - 0.9 ppm: protons in methyl groups not adjoining aromatics directly or in beta-position on them;

1.2 - 1.5 ppm: protons in methylene and methine groups not adjoining aromatics directly or in beta-position on them;

Approx. 2.5 ppm: protons in all alkyl groups on aromatics;

2.5 - 4.5 ppm: protons in methylene and methine groups in bridges between aromatics.

7 - 8 ppm: aromatic protons, protons in phenolic hydroxyl groups.

These assignments correspond to those by other authors. - Also, it is likely from the spectra that some groups are present only in small numbers. This applies to all olefinic protons on carbon atoms whose signals should appear at 4.5 - 6 ppm. In this region, weak signals appear virtually only in the low-temperature tar spectra. A few other groupings might occur, but they cannot be identified qualitatively in the spectra, as for example groupings with triple carbon bonds. Moreover, signal width does not allow more detailed differentiations. For instance, according to the assignment table, there should be some difference between methylene groups in paraffins and those in naphthenes. Although most spectra show signal asymmetry in the 1.0 - 2.0 ppm range, at 1.7 ppm, this finding is not sufficiently conclusive for definite evaluation. According to BARTLE & SMITH (1) the fact that in the range around 1.5 ppm even methyl groups in beta-position on aromatics can absorb appears to be of secondary importance. - Some qualitative information can be drawn from signal form. This applies in particular to the range of aromatic protons. Already TSCHAMLER & OTH (15) and LAHIRI et al. (11) interpreted signal asymmetry at 7 - 9 ppm as the effect of different positions of substituents on the aromatic ring or different linkages between aromatic rings. POPLE, SCHNEIDER & BERNSTEIN (14 a) pointed out that the chemical shifts in the protons of pure condensed aromatics may differ by as much as 2 ppm in dependence on position within the molecule. This is not the place to discuss the theoretical basis of these effects, but we can say that width and asymmetry of the signal of aromatic protons are caused by differences in the type of

aromatics, type and location of substituents, type and number of linkages between aromatic rings as well as effects of heteroatoms on or in the rings. No differentiated statements are possible because of the multitude of various possible effects. If the type of aromatic had a dominating influence it could be assumed that a tendency towards absorption at higher values is due to noticeable fractions of higher-condensed aromatics. For instance, the signal with the greatest shift with regard to TMS is at 8.25 ppm for anthracene, at 8.38 ppm for phenanthrene, at 9.22 ppm for 1,2-benzanthracene, and at 9.60 ppm for 3,4-benzphenanthrene. We can see from the chloroform extract spectra for example that only the extracts of higher-rank coals produce noticeable signals above 9 ppm. Also, we find that in this series of extracts the location of the signal maxima shifts from about 7.8 ppm for extracts of higher-rank coals to about 7.3 ppm for extracts of lower-rank coals; this applies also to the chloroform-soluble fractions of the pyridine extracts. From all this it can at least be concluded that the type of aromatics in extracts is not independent of the volatiles content of the original coals.

Basis of quantitative analysis

The spectra recorded by us can be evaluated quantitatively only through determining the areas under the lines. If the spectrometer is properly adjusted, the areas are directly proportional to the number of protons present in the group being analyzed.

For substances of the kind examined here it is also important to know whether the sample to be analyzed has dissolved completely. Appearance and behaviour of the solutions and the fact

that the area ratios determined for some substances are largely independent of concentration indicate that there is no appreciable adulteration.

A difficult aspect of quantitative evaluation is the division of areas under the lines. Since symmetry or course according to a certain function cannot be given for the various individual signal ranges from the start, the graphical separation into individual signals will contain an arbitrary element. What remains is basing the delimitation of ranges on the minima distinctly visible in the spectra. In connection with the assignment ranges discussed above we are above all interested in the minima at 1.0 and 1.8 - 2.0 ppm occurring clearly in all spectra. It is above all the first minimum (at 1.0 ppm) that makes it improbable that the delimitation of ranges can be done reliably, since the intensity of the first maximum (at 0.8 ppm) is only slightly higher than the minimum, the intensity of the second maximum (at approx. 1.3 ppm) is only about twice as high as that of the minimum. The situation is very similar in the case of higher-boiling saturated mineral oil fractions the average molecular weights of which are comparable to those of the substances investigated here. Recently it was found (12,13) that for such mineral oil fractions, separating the two signals at 0.8 and 1.3 ppm by the perpendicular on the background that intersects at the minimum can ensure correct evaluation of the two areas. Assuming that the situation is similar for the substances investigated here, this method of delimitating signal ranges appears to be justified. The second minimum at 1.8 - 2.0 ppm, for one thing, is less intense than the adjoining maxima, for another, the distance to the adjoining maxima is greater, and consequently it is again admissible to delimit the ranges in this manner. In most cases the intensity drops down as far as the base

line between the maxima at approx. 2.5 ppm and at 7-8 ppm. This makes exact delimitation of ranges possible. For some substances, particularly for low-temperature tars, yet another minimum occurs between 3-4 ppm which was used for evaluation. - As suggested by JACKMANN (8), the individual areas under the lines are measured with a planimeter and related to the sum total of areas.

Derivation of combined IR-NMR group analysis

By combination with the hydrogen contents determined by elemental analysis, the proton fractions in the various groups are obtained in absolute values [percent H_i (waf)]. The fraction of aromatic hydrogen requires correction. Various authors have pointed out that the protons of phenolic hydroxyl groups are definitely included in this range. They can be determined in a different manner and have to be deducted. - The studies on coal extracts carried out so far succeeded merely in determining the quantitative ratio between aliphatic and aromatic hydrogen. The more accurate, now definite separation of areas under the peaks permits a more differentiated distinction between various structural groups. The fraction of aromatic hydrogen determinable from the NMR spectrum ought to correspond to that determined with the IR method. Chloroform extracts have been used to compare the results obtained separately by both methods (Table 1). On average the deviations are 0.2% $H_{(waf)}$. In view of the error margins of both methods and the fact that the errors of elemental analysis and of hydroxyl group determination may enter into NMR spectroscopy, the accuracy of determination has to be described as good. Since the results of IR and NMR spectroscopic analyses agree well with each other, data obtained by these two methods can routinely be combined. The resultant analytical possibilities are outlined below.

Table 1. Aromatic hydrogen in chloroform extracts

Substanz (1)		(2) % H_{ar} aus IR-Messung	(3) % H_{ar} aus NMR-Messung	Δ
(4) Chloroformextrakt aus Kohle	K 19	1,92	2,32	0,40
Chloroformextrakt aus Kohle	K 22	1,98	1,95	0,03
Chloroformextrakt aus Kohle	K 23	1,72	2,13	0,41
Chloroformextrakt aus Kohle	K 26	1,97	2,28	0,31
Chloroformextrakt aus Kohle	K 28	1,73	1,87	0,10
Chloroformextrakt aus Kohle	K 34	1,76	1,67	0,09
Chloroformextrakt aus Kohle	K 36	1,32	1,35	0,03
Chloroformextrakt aus Kohle	K 38	1,58	1,12	0,46
Chloroformextrakt aus Kohle	K 41	1,48	1,47	0,01
				$\Delta M = 0,20$

Key: 1 - substance
2 - % H_{ar} from IR measurements
3 - % H_{ar} from NMR measurements
4 - chloroform extract from coal K 19...K 41

Translator's note: In Tables and Figures, where applicable, please read commas as decimal points.

1. IR analysis gives a total value for methyl group hydrogen, NMR analysis a value for hydrogen in non-aromatic methyl groups. The difference is the hydrogen in methyl groups directly on aromatics.

2. NMR analysis gives values for hydrogen in all aromatic alkyl groups. After deducting the fraction determined for aromatic methyl groups we get the hydrogen in aromatic methylene and methine groups.

3. No differentiation between methylene and methine group hydrogen is possible from IR and high-resolution NMR spectra alone, but the relationship between methylene hydrogen and total hydrogen that has been derived from NMR broad-line measurements by LADNER & STACEY (10) can be used for this purpose. According to this method many coals have a methylene hydrogen/methine hydrogen ratio of 2.96:1 which at a relative standard deviation of 13% is sufficiently constant. If we assume that this ratio applies generally also to the extracts from these coals, the hydrogen fractions in non-aromatic methylene and methine groups - $H_{(CH_2;CH)\,al}$ - can be broken down into simple aromatic arrangement $H_{(CH_2;CH)\,\alpha}$ and into bridge positions between aromatic rings $H_{(CH_2;CH)\,\alpha\,B}$.

4. Using the carbon contents determined by elemental analysis, the various hydrogen fractions can be converted into relative carbon percentages according to the following equations:

$$\%\,C_{CH_3\,rel.} = \frac{\%\,H_{CH_3} \cdot 12}{3 \cdot \%\,C_{(waf)}} \cdot 100 = \frac{\%\,H_{CH_3}}{\%\,C_{(waf)}} \cdot 400 \qquad (1)$$

$$\%\,C_{CH_2\,rel.} = \frac{\%\,H_{(CH_2;CH)}\,0{,}75 \cdot 12}{2 \cdot \%\,C_{(waf)}} \cdot 100 = \frac{\%\,H_{(CH_2;CH)}}{\%\,C_{(waf)}} \cdot 450 \qquad (2)$$

$$\%\,C_{CH\,rel.} = \frac{\%\,H_{(CH_2;CH)} \cdot 0{,}25 \cdot 12}{1 \cdot \%\,C_{(waf)}} \cdot 100 = \frac{\%\,H_{(CH_2;CH)}}{\%\,C_{(waf)}} \cdot 300 \qquad (3)$$

$$\%\,C_{CH\,ar\,rel.} = \frac{\%\,H_{ar\,(korr.)} \cdot 12}{1 \cdot \%\,C_{(waf)}} \cdot 100 = \frac{\%\,H_{ar\,korr.}}{\%\,C_{(waf)}} \cdot 1200 \qquad (4)$$

The correlation for the fraction % C_{OH} is analogous to equation (4).

5. The substituted aromatic carbon fraction is obtained by totalling all carbon contents in aromatic alkyl groups, phenolic hydroxyl groups, and including the quinoid rings in the aromatic carbon fraction in quinoid carbonyl groups. We get

$$\%\,C_{ar\,(sub)} = \%\,C_{CH_3\,a} + \%\,C_{CH_2\,a} + \%\,C_{CH\,a} + 2 \cdot \%\,C_{CH_2\,a\,B} + 3 \cdot \%\,C_{CH\,a\,B}\ \%\,C_{C-OH}\ \%\,C_{C=O\,(quin)} \qquad (5)$$

We should add by way of explanation that a methylene group forming a bridge between aromatic rings substitutes for two aromatic hydrogen atoms. Methine bridges may replace two or three hydrogen atoms. Equation (6) above uses the presumptive maximum value 3. Since the values of these groups are small, possible errors are presumably negligible.

6. The difference between all determined carbon fractions and 100 may contain the following types of carbon bonds:

$C_{ar(kond)}$: aromatic-angular carbon bond

C_{quart}: aliphatic-quaternary carbon bond

C_x: other carbon or carbon not determinable with our methods.

The C_x fraction can be regarded as negligible. The size of the C_{quart} fraction cannot be asessed and is omitted in our calculations. The remaining carbon is therefore aromatic-angular; it might be too high in view of C_{quart} having been ignored.

From the above data the distribution of carbon among the various bond types can be calculated with almost complete accuracy. - To calculate the carbon in aromatic C—H groups the mean hydrogen fraction values obtained from IR and NMR spectroscopic measurements are used.

Various characteristic parameters can then be derived from the resultant data on carbon bond distribution. These parameters have been listed in Table 2. Even earlier studies had used them but in most cases they had been determined on the basis of estimated carbon bond distributions. With the combined IR/NMR analysis method they can be calculated from experimentally determined values. It is particularly from the theoretical maximum of the aromatic H/C ratio and the quotient of type of aromatic compound that the existing mean type of condensation of aromatic structure can be inferred. The values calculated for the various types have been summarized in Table 3. Assuming that a certain type is linked to a molecular chain by C—C bonds, the aromatic type quotient decreases by a characteristic amount for every new member of the polyaryl system. The ratios for several types have been represented in Figure 3.

Examples of application

In the following we will describe the results obtained for a number of chloroform extracts from bituminous Ruhr coals. The volatiles contents of the original coals before extraction were used as reference for the contents of various fractions. Table 4 lists the NMR spectroscopic measurements and the hydrogen distributions calculated with an IR spectroscopic method that was described in detail in an earlier paper published in this Journal[1]. Table 5 shows the distribution of various types of carbon bonds determined by IR/NMR analysis, Table 6 the parameters derived from those data.

The results can be interpreted as follows:

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[1] This Journal, volume 231, 1967, p. 81

Table 2. Derived parameters

Bezeichnung (1)	Berechnung (2)
Aromatizität (3)	$fa = \frac{C_{CH\,ar} + C_{ar\,sub.} + C_{ar\,kond.}}{100}$
Aromatischer Substitutionsindex (4)	$S_{ar} = \frac{C_{ar\,sub.} + C_{ar\,kond.}}{C_{ar\,sub.} + C_{ar\,kond.} + C_{CH\,ar}}$
Substitutionsgrad (5)	$\sigma = \frac{C_{ar\,sub.}}{C_{ar\,sub.} + C_{CH\,ar}}$
Theoretischer Maximalwert des aromatischen H/C-Verhältnis (6)	$\frac{H_{aru}}{C_{ar}} = \frac{C_{CH\,ar} + C_{ar\,sub.}}{C_{ar\,kond.}}$
Aromatentypquotient (7)	$Ty(ar) = \frac{C_{CH\,ar} + C_{ar\,sub.}}{C_{ar\,kond.}}$
Mittlere Zusammensetzung der nicht aromatenständigen Aliphatengruppe (8)	$CH_{i\,al} = \frac{3 \cdot C_{CH_3} + 2 \cdot C_{CH_2} + C_{CH}}{C_{CH_3} + C_{CH_2} + C_{CH}}$
Mittlere Zusammensetzung der aromatenständigen Aliphatengruppe (9)	$CH_i = \frac{3 \cdot C_{CH_3\,a} + 2\,(C_{CH_2\,a} + C_{CH_2\,aB}) + C_{CH\,a} + C_{CH\,aB}}{C_{CH_3\,a} + C_{CH_3\,a} + C_{CH\,a} + C_{CH_3\,aB} + C_{CH\,aB}}$

Key: 1 - parameter
2 - calculation
3 - aromaticity
4 - aromatic substitution index
5 - degree of substitution
6 - theoretical maximum of aromatic H/C ratio
7 - aromatic type quotient
8 - mean composition of non-aromatic aliphatic group
9 - mean composition of aromatic aliphatic group

kond. = condensed

Table 3. Characteristic data of carbon skeleton of various types of aromatics

	Substanz ①	Zahl der kond. Ringe ②	Kondensationstyp ③	Kondens. Typ-Index Ty(ar) ④	theor. H/C-Verhältnis ⑤
6	Benzol	–	–	∞	1,000
7	9,10-Dihydro-anthracen	–	–	∞	1,000
8	5,12-Dihydro-tetracen	2	kata	8,000	0,875
9	Tetrahydrofluoranthen	2	polyaryl	5,000	0,833
10	Diphenyl; Fluoren	2	polyaryl(kata)	5,000	0,833
11	Acenaphthen;	2	kata	4,000	0,800
12	Chinolin	2	kata	3,500	0,778
13	Phenylnaphthalin	3	kata	3,000	0,750
14	Triphenylbenzol	4	polyaryl	3,000	0,750
15	Rubren	8	gem. kata	2,800	0,737
16	Anthracen; Phenanthren	3	kata	2,500	0,715
17	3,4,5,6-Dibenz-fluoren	4	gem. kata	2,330	0,700
18	Acridin	3	kata	2,250	0,693
19	Chrysen	4	kata	2,000	0,667
20	Benzanthracen	4	kata	2,000	0,667
21	Tetracen	4	kata	2,000	0,667
22	Triphenylen	4	kata	2,000	0,667
23	Biphenylen	2	polyary-2	2,000	0,667
24	Fluoranthen	3	gem. kata	2,000	0,625
25	Benzanthracen	4	kata-peri	1,830	0,647
26	Picen	5	kata	1,750	0,637
27	Pentacen	5	kata	1,750	0,637
28	Benzofluoranthen	4	kata	1,710	0,600
29	Benzfluoren	3	gem. kata	1,670	0,625
30	Pyren	4	peri	1,670	0,625
31	Hexacen	6	kata	1,600	0,615
32	Heptacen	7	kata	1,500	0,600
33	Benzpyren	5	peri	1,500	0,600
34	Perylen	5	peri	1,500	0,600
35	Tribenzpyren	7	kata-peri	1,333	0,571
36	1,12-Benzperylen	6	peri	1,200	0,546
37	Rubicen	5	gem. kata	1,166	0,538
38	Coronen	7	peri	1,000	0,500
39	1,2-Benzcoronen	8	peri	1,000	0,500
40	Peritlanthen	7	peri	1,000	0,500
41	2,3,8,9-Dibenzcoronen	9	peri	0,875	0,467
42	Hexabenzcoronen	13	peri	0,750	0,429

For translation key please see p. 18.

Translation key for Table 3

1 - substance
2 - number of condensed rings
3 - type of condensation
4 - condensation type index
5 - theoretical H/C ratio
6 - benzene
7 - 9,10-dihydroanthracene
8 - 5,12-dihydrotetracene
9 - tetrahydrofluoranthene
10 - diphenyl; fluorene
11 - acenaphthene
12 - quinoline
13 - phenylnaphthalene
14 - triphenylbenzene
15 - rubrene
16 - anthracene; phenanthrene
17 - 3,4,5,6-dibenzofluorene
18 - acridine
19 - chrysene
20 - benzanthracene
21 - tetracene
22 - triphenylene
23 - biphenylene
24 - fluoranthene
25 - benzanthracene
26 - picene
27 - pentacene
28 - benzofluoranthene
29 - benzofluorene
30 - pyrene
31 - hexacene
32 - heptacene
33 - benzpyrene
34 - perylene
35 - tribenzpyrene
36 - 1,12-benzoperylene
37 - rubicene
38 - coronene
39 - 1,2-benzocoronene
40 - periflanthene
41 - 2,3,8,9-dibenzocoronene
42 - hexabenzocoronene

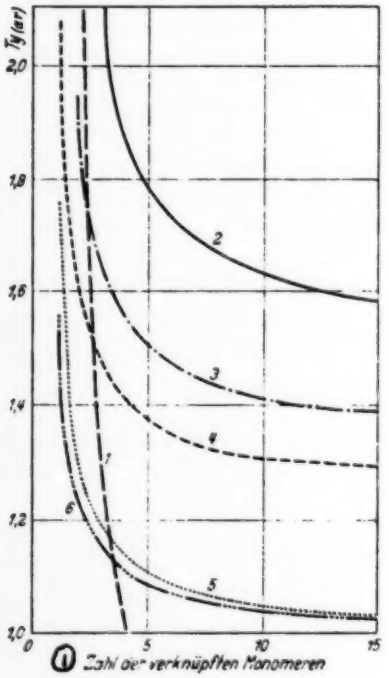

Figure 3. Aromatic type index of various aromatics in dependence on number of building blocks in polyaryl system

1 - benzene (double linkage, biphenylene type)
2 - naphthalene, acenaphthene
3 - anthracene, phenanthrene
4 - chrysene, triphenylene
5 - pyrene, benzofluorene
6 - perylene, benzopyrene

Key: 1 - number of linked monomers

Table 4. Combined IR/NMR group analysis; values obtained for chloroform extracts

Substanz ①	Elementaranalyse %(waf) C	H ②	NMR-Spektrum Flächen-% (rel.) ③ A	B	C	D	E	F	IR-Analyse-% H (abs.) ④ $H_{arom.}$	H_{CH_2}	H_{OH}	%$C_{C=O}$ (abs.)
C 15	86,9	6,25	8,2	21,2	24,9	1,2	44,5		1,90	1,24	0,14	
C 19	86,3	6,30	11,6	21,8	23,2	4,0	39,4		1,92	2,06	0,16	
C 22	89,5	6,90	12,1	22,3	27,6	4,5	33,6		1,98	2,43	0,07	
C 23	87,6	6,77	13,4	27,2	24,4	1,5	33,4		1,72	2,27	0,13	
C 26	88,6	7,00	11,6	25,7	27,1	1,7	34,0		1,97	2,33	0,10	0,4
C 28	88,2	7,00	19,9	31,6	20,7	1,5	26,3		1,73	2,40	0,13	
C 34	86,8	7,10	28,4	30,9	14,8		25,8		1,76	3,03	0,16	
C 36	85,4	7,75	23,0	32,8	21,4	2,4	20,3		1,32	2,83	0,22	0,8
C 38	85,3	6,90	19,8	39,2	21,9		19,1		1,58	3,19	0,20	0,4
C 41	86,2	7,55	17,1	33,2	25,8	1,7	22,1		1,48	2,75	0,20	1,6

A 0→1,0 ppm (Minimum); B 1,0→1,5 ppm
C 1,5→2,0 ppm (Minimum); D 2,0→3,6 ppm (Minimum);
E 3,6→5,8 ppm F 5,8→10,0 ppm

Key: 1 - substance
2 - elemental analysis, % (waf)
3 - NMR spectrum, % area under peak (rel.)
4 - IR analysis, % H (abs.)

Table 5. Combined IR/NMR group analysis; relative carbon distribution in chloroform extracts

Substanz (1)	%-C rel												
	aliphatisch (2)			aromatenständig (3)					O-haltig aromatisch (4)		aromatisch (5)		
	CH_3	CH_2	CH	CH_3	CH_2	CH	$CH_{2(Br)}$	$CH_{(Br)}$	C_{C-OH}	$C_{C=O}$	C_{CH}	$C_{sub.}$	$C_{kond.}$
C 15	2,3	6,9	4,6	3,4	4,3	2,9	0,4	0,3	1,9		31,4	14,2	27,4
C 19	3,4	7,1	4,8	6,2	0,7	0,5	1,3	0,9	2,2		29,5	14,9	28,5
C 22	3,3	6,7	4,5	7,6			1,4	0,9	0,9		26,4	14,0	34,3
C 23	4,2	9,5	6,3	6,2	1,5	1,0	0,5	0,3	1,8		26,3	12,4	30,0
C 26	3,7	9,1	6,1	6,9	1,9	1,3	0,6	0,4	1,4	0,4	28,7	14,3	25,2
C 28	6,8	12,2	8,2	4,0	3,5	2,3	0,6	0,4	1,8		24,6	14,6	21,6
C 34	9,3	11,4	7,6	4,7	1,6	1,0			2,2		23,6	9,5	29,1
C 36	8,3	13,4	8,9	4,9	3,2	2,1	1,0	0,7	3,1	0,8	18,8	18,2	16,6
C 38	6,4	14,2	9,5	8,5					2,8	0,4	19,0	11,7	27,5
C 41	6,0	13,1	8,7	6,8	2,6	1,7	0,7	0,5	2,8	1,6	20,4	18,4	16,7

Key: 1 - substance
2 - aliphatic
3 - aromatic
4 - containing oxygen, aromatic
5 - aromatic

Table 6. Parameters for chloroform extracts derived from combined IR/NMR group analysis data

Substanz ①	fa	Sar	σ	$Ty_{(ar)}$	H_{arn} / C_{ar}	C_{al} / C_x	CH^3 (al) i	CH_i (a i
C 15	0,73	0,57	0,31	1,67	0,62	1,22	1,83	2,02
C 19	0,73	0,59	0,34	1,56	0,61	1,59	1,91	2,50
C 22	0,75	0,64	0,35	1,18	0,54	1,46	1,92	2,68
C 23	0,69	0,61	0,32	1,29	0,56	2,16	1,90	2,52
C 26	0,68	0,58	0,33	1,71	0,63	1,70	1,87	2,47
C 28	0,60	0,59	0,36	1,79	0,64	2,52	1,95	2,12
C 34	0,62	0,62	0,29	1,14	0,54	3,88	2,06	2,51
C 36	0,54	0,64	0,49	2,23	0,69	2,57	1,98	2,18
C 38	0,58	0,66	0,38	1,12	0,53	3,54	1,90	3,00
C 41	0,55	0,64	0,47	2,32	0,71	2,26	1,90	2,38
M =	0,65	0,61	0,36	1,60	0,61	2,28	1,92	2,44

Key: 1 - substance

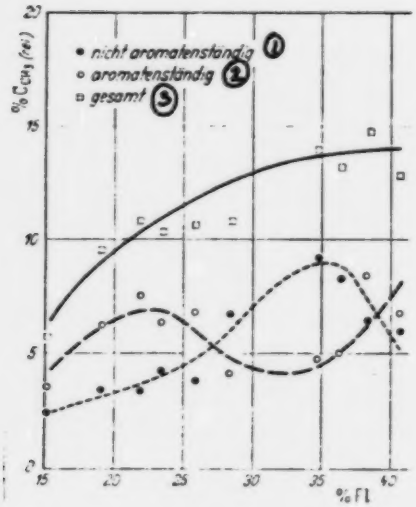

Figure 4

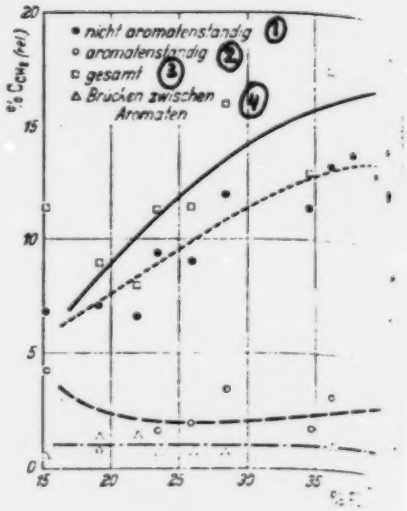

Figure 5

Figure 4. Carbon distribution according to IR/NMR analysis. Methyl group carbon as a function of volatiles content. Chloroform extracts.

Figure 5. Carbon distribution according to IR/NMR analysis. Methylene group carbon as a function of volatiles content. Chloroform extracts.

Key: 1 - non-aromatic
2 - aromatic
3 - total
4 - bridges between aromatics

Fl = volatiles

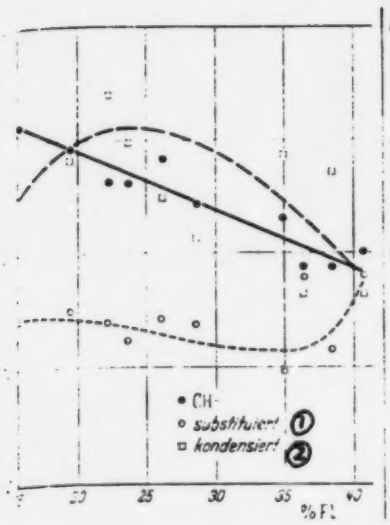

Figure 6

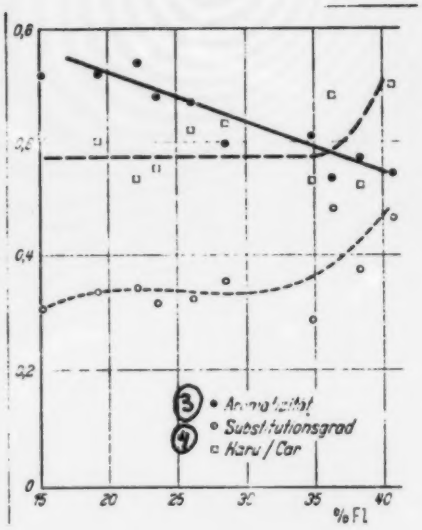

Figure 7

Figure 6. Carbon distribution according to IR/NMR analysis. Aromatic carbon as a function of volatiles content. Chloroform extracts.

Figure 7. IR/NMR analysis. Derived parameters as a function of volatiles content. Chloroform extracts.

Key: 1 - substituted
2 - condensed
3 - aromaticity
4 - degree of substitution

Methyl groups (Figure 4). Extracts from higher-rank coals (up to approx. 27% volatiles) have more aromatic methyl groups. While no uniform course can be observed for the two fractions, the total methyl group fraction rises. Overall, there are about 7 - 14% in methyl groups. There are no published data on chloroform extracts with which our findings could be compared.

Methylene groups (Figure 5). Most of the methylene groups are non-aromatic, and this fraction shows a rising tendency. The fraction of aromatic methylene groups shows no pronounced tendency; it amounts to 15% (extracts from lower-rank coals) to 30% (extracts from higher-rank coals) of the non-aromatic methylene group content. The fraction of methylene groups in bridges between aromatic rings amounts to only approx. 1% and remains constant. The sum of all methylene groups rises from 9 to 16%. As regards the tendencies of methine group fractions, the same holds true in accordance with the assumptions made for the calculations.

Aromatic carbon (Figure 6). Aromatic C—H groups decrease almost linearly from 32% to 19%. The substituted carbon fraction first decreases from 15% to 10% - 12% at volatiles contents of 33 - 35%, then rises again to about 18%. While in extracts from higher-rank coals the CH group fraction is about twice as great as the substituted carbon fraction, the values for extracts from lower-rank coals again move closer together. The values for carbon in angular bonds scatter widely. Overall, they are comparable to the CH group values; there is a falling tendency.

The total content of aromatic carbon is expressed by **aromaticity** (Figure 7) which decreases almost linearly from 0.76 to 0.55. At volatiles contents up to more than 30% the degree of aromatic substitution σ' remains more or less constant at

0.32 - 0.36 and rises up to 0.50 only in extracts from lower-rank coals. The values for the theoretical H/C ratio of non-substituted aromatics (H_{aru} C_{ar}) rise only slightly in one band between 0.55 and 0.68.

The mean aromaticities for chloroform extracts are distinctly lower than for extracts obtained by different methods with usually higher yields.

The degree of substitution is almost identical for all extracts. Slightly more than one third of all possible sites in the aromatic ring have substituents.

Assuming that no direct linkages exist between aromatics in the sense of a polyaryl system, it appears plausible from the mean structural parameters obtained for chloroform extracts that systems with 3-4 condensed rings, for instance of the type of benzofluorene or pyrene, are present. However, the benzofluorene type would require a 16:1 ratio of aromatic carbon relative to carbon in methylene bridges, a ratio which according to our findings does not apply. If, on the other hand, only one linkage between aromatics per molecule is postulated, a hypothesis that has been discussed by v. KREVELEN (9), the extracts would have to contain aromatics of the anthracene or phenanthrene type.

The mean composition of aliphatic groups is $CH_{1\ al}$ = 1.9 for non-aromatic groups, $CH_{1\ a}$ = 2.4 for aromatic groups. Thus there are more methylene groups in the non-aromatic fraction, but more methyl groups in the aromatic fraction.

Experimental

Extraction. The extracts were obtained from the carefully dried coals by 48-h steam extraction in a nitrogen atmosphere.

NMR measurements. The spectra were recorded with a Varian HR 60. Solvent: deuterochloroform; concentrations: 5 - 15%; internal standard: tetramethylsilane. Optimum equipment adjustment was attempted for each measurement. Intensification of the 60-MHz field and rate of magnetic field variation were held constant throughout all measurements. Sample rotation; recording at a rate of 420 sec/ppm. The individual signal ranges of the spectra were measured with a planimeter.

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